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METHODS FOR PREVENTION OF HEATING OF AN ADSORBENT BY INFRARED RADIATION IN STUDIES ON THE SPECTRA OF ADSORBED MOLECULES

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ABSTRACT. A method is discussed for preventing internal heating of an adsorbent in studies on the interaction of adsorbed molecules and the surface in quantitative comparisons of spectral and adsorption data from infrared spectra. Placing the specimen in a resolved beam of infrared radiation, so as to cause a monochromatic light beam to pass through it, will effectively prevent heating. The modified cell, used in the two-beam system of the UR-10 spectrometer, is described.

The most complete information on the interaction between adsorbed molecules and the surface, and on their state, can be obtained from infrared spectra by quantitative comparison of the spectral and adsorption data at known surface coverage of the adsorbed molecules. Until now, however, all spectral studies have neglected the heating of the adsorbent specimen by the infrared radiation, so that the spectral data cannot be quantitatively compared with the data of the adsorption methods, found in most cases at constant and moderate temperatures (generally, room temperature). Most cells for studying the infrared spectra of adsorbed molecules [cf. survey in another paper (Ref.1)] have no provision for measuring the specimen temperature. Cells that cool the specimen are described elsewhere (Ref.2, 3).

The cell shown in Fig.1 was used by us for this work. The cell body (1) was made of molybdenum glass. It had two openings with windows (2) of transparent material, to pass infrared radiation. The windows were pasted to the cell body with BF-2 cement. The inlet tube (4) entered the top of the cell through the ground-glass joint (3). The end of the inlet tube carried a soldered-on closed tube (5) to which the specimen (7) was mounted by means of the holder (6) made of metal foil. The inlet tube was made of quartz. The specimen was heated by the spiral (8) passing through the closed tube (5) of the inlet tube. The specimen was cooled by pouring a coolant into the inlet tube (4). The temperature was determined by a constantan-copper thermocouple introduced into the cell through the branch tube (9). Piceine was used for the vacuum seal. The thermocouple was pressed into the tablet of adsorbent. The specimen could be exhausted at temperatures up to 400°C. The cell body (1), the ground-glass joint (3), and the windows (2) were cooled by water passed through the copper tubes (10) attached to the cell body. Working with this cell in the two-beam system of the

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* Numbers in the margin indicate pagination in the foreign text.

UR-10 spectrometer, the temperature of the specimen could be brought down to 25 - 30°C, the temperature most frequently used in adsorption studies, by putting an ice and water mixture into the inlet tube (4). /741

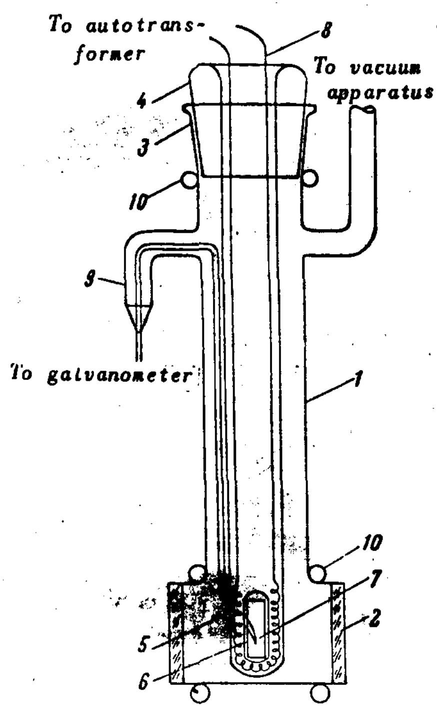

Fig.1 Vacuum Cell for Studying Infrared Spectra of Adsorbed Molecules at Various Determinable Temperatures of the Specimen.

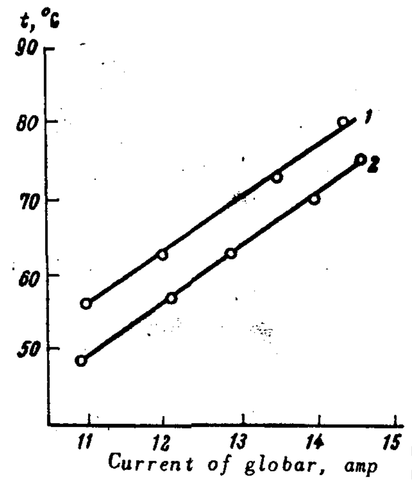

Fig.2 Dependence of Temperature of Pressed Aerosil Tablet Exhausted at: 1 - 25°C or 2 - 400°C on the Current through the Globar of the Spectrometer.

In taking spectra without cooling, we found that the specimen was strongly heated by the infrared beam. The extent of heating depended on the current passing through the globar. Figure 2 is a plot of the temperature of a platelet of Aerosil (silica powder) placed in the cell (Fig.1) versus the current through the globar of the UR-10 infrared spectrometer. This graph shows that the temperature of the specimen under ordinary operating conditions (globar current, 13 - 14 amp) is 70 - 80°C and depends strongly on both the globar current and the specimen preparation. Exhaustion of the specimen at 400°C decreases the heating by removing the adsorbed water and a considerable part of the surface hydroxyl groups (Ref.4) whose valence vibrations yield absorption bands closest to the region of maximum power of the globar radiation.

The accompanying table shows that the heating of the specimen during adsorption is likewise determined by the convective removal of heat and depends on the vapor pressure of the adsorbed substance in the cell. Introduction of benzene vapor into the cell causes a rapid rise in the specimen temperature; this rise then slows down as a result of heat removal by convection. This current dependence of the specimen temperature is particularly distinct when the

DEPENDENCE OF THE TEMPERATURE OF A PRESSED AEROSIL TABLET AND OF η, THE PROPORTION OF HYDROXYL GROUPS PARTICIPATING IN THE REACTION, ON THE CURRENT THROUGH THE GLOBAR AND THE VAPOR PRESSURE OF BENZENE IN THE CELL

p	t_1 at $I = 11$ amp	t_2 at $I = 14$ amp	t_3 (Additional Heating)	η_1	η_2	η_3	$\eta_{20°}$
7.7	44	60	88.5	0.24	0.16	0.07	0.50
17.8	45.5	62.5	89	0.36	0.28	0.13	0.75
80	47.5	64.5	82	0.7	0.52	0.45	1.0

heater (8) is used (Table). In this case, despite the increase in adsorption and the accompanying increase in absorption of the energy of the infrared radiation at higher relative pressures of the benzene vapor, a decline in specimen temperature is noted.

An increase in specimen temperature has a strong effect on the adsorptive equilibrium (the surface concentration of the adsorbate declining sharply) and is distinctly manifest in the decreased proportion η of hydroxyl groups participating in the interaction with the adsorbed molecules (see the table). The quantity η is defined as the ratio of the number of hydroxyl groups interacting with the adsorbed molecules /742 (difference in intensity of the 3749 cm^{-1} absorption band before and after adsorption) to their total number (original intensity).

Preventing the heating of the specimen by additional cooling with a coolant (Fig.1) does not overcome all difficulties of a combined study of spectral and adsorption properties. With such cooling, the walls of the inlet tube (4) will be at a temperature lower than that of the specimen (Fig.1) so that the vapors of many substances may condense there and pass into the liquid or solid state. A low equilibrium pressure of the vapor with this state is then established, adsorption decreases, and adsorptive equilibrium is established very slowly.

Strong heating of the specimen may be prevented by interposing a filter between radiation source and specimen, with absorption in the region of maximum radiation of the globar. It is difficult, however, to select a filter that will prevent heating without simultaneously absorbing radiation in the working region of the spectrum.

The most convenient method of preventing heating and permitting a study of the spectra of adsorbed substances at room temperature is to place the specimen in a resolved beam of infrared radiation, so that a monochromatic light beam will pass through it. McDonald calls attention to the possibility of using this method (Ref.5). However, use of this single-beam system requires rebuilding the instrument and imposes many restrictions, due mainly to having to work with a single-beam system and the consequent lack of compensation of absorption by the vapor of the atmosphere. Special difficulties arise in studying the region of absorption of hydroxyl groups. The strong absorption by atmospheric water vapor and the water vapor inside the LiF prism makes it necessary to deuterize the specimen and to then study the spectrum of the deuterium-substituted substances.

If the UR-10 spectrometer is used and the specimen is placed in a beam of resolved light, operating on the single-beam principle, the cover of the thermostated part of the spectrometer must be replaced by a new one with an opening into which the cell is introduced, with the specimen centered relative to the beam after the exit slit of the monochromator.

The resultant values for η, the proportion of hydroxyl groups on the surface participating in the interaction with the adsorbed molecules (table), are closest to the results of adsorption measurements.

Conclusions

In studying infrared spectra in a two-beam system, the specimen of adsorbent is heated to 70 - 80°C. The heating of the specimen depends on the kind and number of adsorbed molecules. Heating of the specimen is completely avoided by placing it in a monochromatic beam.

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